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**UNITED STATES PATENT APPLICATION**

**OF**

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**FOR**

**COSMETIC COMPOSITIONS COMPRISING**

**AT LEAST ONE SILICONE COPOLYMER AND**

**AT LEAST ONE ADDITIONAL SILICONE, AND USES THEREOF**

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The present invention relates to novel cosmetic compositions comprising, in a cosmetically acceptable medium, at least one silicone copolymer defined below, with a dynamic viscosity ranging from  $1 \times 10^6$  to  $100 \times 10^6$  cP and at least one additional silicone.

5 It is well known that hair that has been sensitized (i.e. damaged and/or embrittled) to varying degrees under the action of atmospheric agents or mechanical or chemical treatments, such as dyes, bleaches and/or permanent-waving, can be often difficult to disentangle and to style, and may lack softness.

10 It has already been recommended to use conditioners, in particular cationic polymers or silicones, in compositions for washing or caring for keratin materials such as the hair, in order to facilitate the disentangling of the hair and to give it softness and suppleness. However, the cosmetic advantages mentioned above can be accompanied, on dried hair, by certain cosmetic effects considered undesirable, i.e., lankness of the hairstyle (lack of lightness of the hair) and lack of smoothness (hair not  
15 uniform from the root to the tip).

In addition, the use of cationic polymers for this purpose may have various drawbacks. On account of their high affinity for the hair, some of these polymers can become deposited thereon to a large extent during repeated use, and may lead to adverse effects such as an unpleasant, laden feel, stiffening of the hair and interfiber  
20 adhesion which may affect styling. These drawbacks may be more accentuated in the case of fine hair, which lacks liveliness and body.

In summary, it is found that the current cosmetic compositions comprising cationic silicones and/or cationic surfactants are not always entirely satisfactory.

The inventors have now discovered that the combination of at least one silicone copolymer defined below, with a dynamic viscosity ranging from  $1 \times 10^6$  to  $100 \times 10^6$  cP, with at least one additional silicone makes it possible to overcome at least one of these drawbacks.

Thus, after considerable research conducted in this matter, the inventors have found that by introducing at least one silicone copolymer with a dynamic viscosity ranging from  $1 \times 10^6$  to  $100 \times 10^6$  cP, into compositions, such as hair compositions containing at least one additional silicone, it is possible to limit, or even eliminate, the problems generally associated with the use of such compositions, i.e., for example, the lankness (charged feel following repeated applications) and the lack of smoothness and softness of the hair, while at the same time retaining at least one of the other advantageous cosmetic properties which are associated with conditioner-based compositions.

Moreover, when applied to the skin, for example in the form of a bubble bath or shower gel, the compositions of the invention can provide an improvement in the softness of the skin.

Thus, according to the present invention, cosmetic compositions are now proposed comprising, in a cosmetically acceptable medium, at least one silicone copolymer defined below, wherein said copolymer has a dynamic viscosity ranging from  $1 \times 10^6$  to  $100 \times 10^6$  cP, and at least one additional silicone.

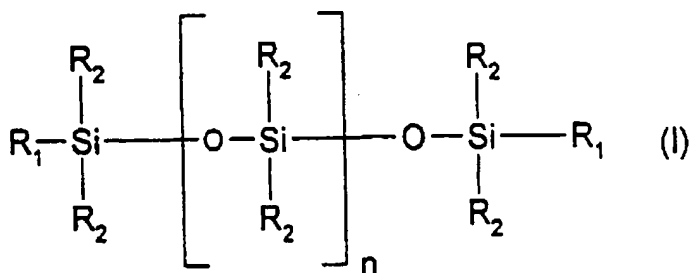
Another subject of the invention relates to the use of at least one silicone copolymer defined below, with a dynamic viscosity ranging from  $1 \times 10^6$  to  $100 \times 10^6$  cP,

in, or for the manufacture of, a cosmetic composition comprising at least one additional silicone.

The various subjects of the invention will now be described in detail. All the meanings and definitions of the compounds used in the present invention given below are valid for all the subjects of the invention.

The at least one silicone copolymer results from the addition reaction, in the presence of a catalyst, of at least:

- (a) one polysiloxane of formula (I):



in which:

-  $R_1$ , which may be identical or different, are independently chosen from groups that can react by chain addition reaction such as, for example, a hydrogen atom or aliphatic groups comprising an ethylenic unsaturation, such as vinyl, allyl and hexenyl groups;

-  $R_2$  in formula (I), which may be identical or different, are independently chosen from alkyl, alkenyl, cycloalkyl, aryl, hydroxyl, and alkylaryl groups, and can optionally further comprise functional groups chosen from ethers, amines, carboxyls, hydroxyls, thiols, esters, sulfonates and sulfates; wherein:

- the alkyl groups comprise, for example, 1 to 20 carbon atoms; the alkenyl groups comprise, for example, from 2 to 10 carbon atoms; the cycloalkyl groups comprise, for example, 5 or 6 carbon atoms; the aryl groups comprise, for example, phenyl groups; and the alkylaryl groups comprise, for example, from 7 to 20 carbon atoms;

- In one embodiment,  $R_2$  is chosen from methyl.

-  $n$  is an integer wherein the polysiloxane of formula (I) has a kinematic viscosity ranging from 1 to  $1 \times 10^6$  mm<sup>2</sup>/s, for example,  $n$  may range from 5 to 5000; and

- (b) at least one silicone compound comprising at least one and not more than two groups capable of reacting with the groups  $R_1$  of the polysiloxane (a), wherein:

- at least one of the compounds of type (a) and (b) comprises an aliphatic group, such as a  $C_2$ - $C_6$  aliphatic group, comprising an ethylenic unsaturation.

The compounds of type (b) can be another polysiloxane of type (a) in which at least one and not more than two groups  $R_1$  of the polysiloxane (b) can react with the groups  $R_1$  of the polysiloxane (a).

In one embodiment, the at least one silicone copolymer is obtained by addition reaction, in the presence of a hydrosilylation catalyst (for example a platinum catalyst), of at least:

- (a) one  $\alpha,\omega$ -divinylpolydimethylsiloxane, and
- (b) one  $\alpha,\omega$ -dihydrogenopolydimethylsiloxane.

The silicone copolymer generally has a dynamic viscosity, measured at a temperature of about 25°C and at a shear rate of 0.01 Hz for a stress of 1500 Pa, ranging from  $1 \times 10^6$  to  $100 \times 10^6$  cP, such as ranging from  $5 \times 10^6$  cP to  $30 \times 10^6$  cP.

All the dynamic viscosity measurements given in the present patent application were taken at a temperature of about 25°C, on a Carri-Medium CSL2-500 machine.

The kinematic viscosity is measured, for example, at 25°C according to ASTM standard 445 Appendix C.

5           The at least one silicone copolymer according to the invention is essentially non-crosslinked, i.e., not crosslinked to an extent sufficient to be referred to as a crosslinked copolymer.

Another subject of the invention relates to compositions wherein the at least one silicone copolymer present in the composition is in the form of an aqueous emulsion.

10           The expression "aqueous emulsion" means an emulsion of oil-in-water type in which the at least one silicone copolymer is dispersed, such as in the form of particles or droplets, in the aqueous phase forming the continuous phase of the emulsion. This emulsion can be stabilized with a common emulsifying system.

15           This silicone emulsion can have a silicone droplet or particle size ranging from 10 nm to 50  $\mu\text{m}$ , such as from 0.3  $\mu\text{m}$  to 20  $\mu\text{m}$ . The particle size is measured by laser granulometry.

The emulsifying system comprises at least one surfactant commonly used in silicone emulsions. These surfactants may be nonionic, cationic, anionic or amphoteric, or mixtures thereof, such as those described below.

20           The emulsifying system represents, for example, from 0.5% to 10% by weight relative to the total weight of the emulsion.

The synthesis of these silicone emulsions is described for example in patent application EP-A-874 017, the disclosure of which is incorporated by reference herein.

Such emulsions are sold for example under the name DC2-1997 Cationic Emulsion by the company Dow Corning. This emulsion comprises an  $\alpha,\omega$ -divinyl-dimethicone/ $\alpha,\omega$ -dihydrogenodimethicone copolymer with a dynamic viscosity of about  $15 \times 10^6$  cP, an emulsifier of cationic type such as cetyltrimethylammonium chloride, a stabilizer such as hydroxyethylcellulose, and water.

The at least one silicone copolymer can be present in a representative amount ranging from 0.05% to 10% by weight relative to the total weight of the composition, such as from 0.1% to 5% by weight relative to the total weight of the composition.

The aqueous emulsion of the at least one silicone copolymer can be present in a representative amount ranging from 0.5% to 15% by weight relative to the total weight of the composition.

The silicones, other than the silicone copolymer of the invention defined above that can be used in accordance with the invention can, for example, be chosen from polyorganosiloxanes that are insoluble in the composition and that can be chosen from oils, waxes, resins and gums.

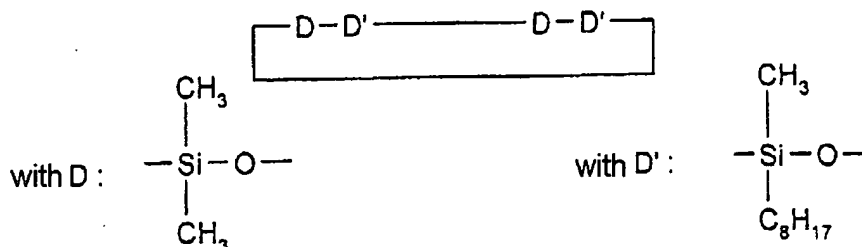
Such polyorganosiloxanes, which can be volatile or non-volatile, are defined in greater detail in the book by Walter Noll "Chemistry and Technology of Silicones" (1968) Academic Press.

Volatile polyorganosiloxanes can be chosen from those having a boiling point ranging from 60°C to 260°C, and, for example, chosen from:

(i) cyclic polyorganosiloxanes comprising from 3 to 7 and preferably from 4 to 5 silicon atoms. Such polyorganosiloxanes, for example, can be chosen from at least one octamethylcyclotetrasiloxane, sold for example under the name "Volatile Silicone 7207"

by Union Carbide, and "Silbione 70045 V 2" by Rhône-Poulenc; and  
 decamethylcyclotetrasiloxane, sold under the name "Volatile Silicone 7158" by Union  
 Carbide, and "Silbione 70045 V 5" by Rhône-Poulenc.

Mention may also be made of cyclocopolymers of the  
 5 dimethylsiloxane/methylalkylsiloxane type, such as "Volatile Silicone FZ 3109" sold by  
 the company Union Carbide, of chemical structure:



10 Mention may also be made of mixtures of cyclic polyorganosiloxanes with  
 organosilicon compounds, such as the mixture of octamethylcyclotetrasiloxane and  
 tetratrimethylsilylpentaerythritol, such as a 50/50 mixture, and the mixture of  
 octamethylcyclotetrasiloxane and oxy-1,1'-bis(2,2,2',2',3,3'-  
 hexatrimethylsilyloxy)neopentane;

15 (ii) linear volatile polyorganosiloxanes comprising from 2 to 9 silicon atoms with a  
 kinematic viscosity of less than or equal to  $5 \times 10^{-6} \text{ m}^2/\text{s}$  at  $25^\circ\text{C}$ . This is, for example,  
 decamethyltetrasiloxane, sold for example under the name "SH 200" by the company  
 Toray Silicone. Silicones forming part of this category are also described in the article

published in Cosmetics and Toiletries, Vol. 91, Jan. 76, pp. 27-32, Todd & Byers  
"Volatile Silicone Fluids for Cosmetics".

Non-volatile polyorganosiloxanes that can be used are chosen from  
polyalkylsiloxanes, polyarylsiloxanes, polyalkylarylsiloxanes, silicone gums, silicone  
5 resins, and polyorganosiloxanes modified with organofunctional groups, and mixtures  
thereof.

Non-volatile silicones are, for example, chosen from polyalkylsiloxanes, such as  
polydimethylsiloxanes that comprise trimethylsilyl end groups with a kinematic viscosity  
of from  $5 \times 10^{-6}$  to  $2.5 \text{ m}^2/\text{s}$  at  $25^\circ\text{C}$ , such as from  $1 \times 10^{-5}$  to  $1 \text{ m}^2/\text{s}$ . The kinematic  
10 viscosity of the silicones is measured, for example, at  $25^\circ\text{C}$  according to  
ASTM standard 445 Appendix C.

Among these polyalkylsiloxanes, mention may be made, in a non-limiting  
manner, of the following commercial products:

- the Silbione oils of the series 47 and 70 047 and the Mirasil oils sold by Rhône-  
15 Poulenc, such as, for example, the oil 70 047 V 500 000;
- the oils of the Mirasil series sold by the company Rhône-Poulenc;
- the oils of the 200 series from the company Dow Corning, such as, for example,  
DC200 with a viscosity of 60,000 Cst; and
- the Viscasil oils from General Electric and certain oils of the SF series (SF 96, SF 18)  
20 from General Electric.

Mention may also be made of polydimethyl-siloxanes comprising dimethylsilanol  
end groups (Dimethiconol according to the name given in the International Cosmetic

Ingredient Dictionary and Handbook, hereafter "CTFA"), such as the oils of the 48 series from the company Rhône-Poulenc.

In this category of polyalkylsiloxanes, mention may also be made of the products sold under the names "Abil Wax 9800 and 9801" by the company Goldschmidt, which are poly(C<sub>1</sub>-C<sub>20</sub>)alkylsiloxanes.

The polyalkylarylsiloxanes can be chosen, for example, from linear and branched polydimethyl-methylphenylsiloxanes and polydimethyldiphenylsiloxanes with a kinematic viscosity of from  $1 \times 10^{-5}$  to  $5 \times 10^{-2}$  m<sup>2</sup>/s at 25°C.

Among these polyalkylarylsiloxanes, mention may be made, by way of example, of the products sold under the following names:

- the Silbione oils of the 70 641 series from Rhône-Poulenc;
- the oils of the Rhodorsil 70 633 and 763 series from Rhône-Poulenc;
- the oil Dow Corning 556 Cosmetic Grade Fluid from Dow Corning;
- the silicones of the PK series from Bayer, such as the product PK20;
- the silicones of the PN and PH series from Bayer, such as the products PN1000 and PH1000;
- certain oils of the SF series from General Electric, such as SF 1023, SF 1154, SF 1250 and SF 1265.

Additionally, at least one silicone gum can be used in accordance with the invention. For example, polydiorganosiloxanes with high number-average molecular masses ranging from 200,000 and 1,000,000 can be used. When more than one silicone gum is used, at least one solvent chosen from volatile silicones,

polydimethylsiloxane (PDMS) oils, polyphenylmethylsiloxane (PPMS) oils, isoparaffins, polyisobutylenes, methylene chloride, pentane, dodecane and tridecane is also used.

Mention may be made, for example, of the following products:

- polydimethylsiloxane,
- polydimethylsiloxane/methylvinylsiloxane gums,
- polydimethylsiloxane/diphenylsiloxane,
- polydimethylsiloxane/phenylmethylsiloxane, and
- polydimethylsiloxane/diphenylsiloxane/methylvinyl-siloxane.

Products which can be used, for example, in accordance with the invention are mixtures such as:

- mixtures formed from a polydimethylsiloxane hydroxylated at the end of the chain (referred to as dimethiconol according to the nomenclature in the CTFA dictionary) and from a cyclic polydimethylsiloxane (referred to as cyclomethicone according to the nomenclature in the CTFA dictionary), such as the product Q2 1401 sold by the company Dow Corning;
- mixtures formed from a polydimethylsiloxane gum and from a cyclic silicone, such as the product SF 1214 Silicone Fluid from the company General Electric; this product is an SF 30 gum corresponding to a dimethicone, having a number-average molecular weight of 500,000, dissolved in SF 1202 Silicone Fluid oil corresponding to decamethylcyclopentasiloxane;
- mixtures of two PDMSs of different viscosities, and for example of a PDMS gum and a PDMS oil, such as the product SF 1236 from the company General Electric. The product SF 1236 is a mixture of a gum SE 30 defined above,

having a kinematic viscosity of 20 m<sup>2</sup>/s, and an oil SF 96, with a kinematic viscosity of 5 x 10<sup>-6</sup> m<sup>2</sup>/s. This product preferably contains 15% SE 30 gum and 85% SF 96 oil.

The organopolysiloxane resins which can be used in accordance with the invention are crosslinked siloxane systems comprising units chosen from:  
5 R<sub>2</sub>SiO<sub>2/2</sub>, R<sub>3</sub>SiO<sub>1/2</sub>, RSiO<sub>3/2</sub> and SiO<sub>4/2</sub> in which R is chosen from hydrocarbons comprising from 1 to 16 carbon atoms and phenyl groups. For example, the products in which R is chosen from C<sub>1</sub>-C<sub>4</sub> alkyls can be used. And more specifically, R can be chosen from methyl, and phenyl groups.

10 Among these resins, mention may be made of the product sold under the name "Dow Corning 593" and those sold under the names "Silicone Fluid SS 4230 and SS 4267" by the company General Electric, and which are silicones of dimethyl/trimethyl siloxane structure.

15 Mention may also be made of the resins of the trimethylsiloxysilicate type sold for example under the names X22-4914, X21-5034 and X21-5037 by the company Shin-Etsu.

The organomodified silicones which can be used in accordance with the invention are silicones such as defined above comprising at least one organofunctional group attached by way of divalent hydrocarbon radicals.

20 Among the organomodified silicones, mention may be made of polyorganosiloxanes comprising:

- at least one group chosen from polyethylenoxy and polypropylenoxy groups optionally comprising C<sub>6</sub>-C<sub>24</sub> alkyl groups, such as the products known as

dimethicone copolyol sold by the company Dow Corning under the name DC 1248, and the oils Silwet L 722, L 7500, L 77 and L 711 from the company Union Carbide, and the (C<sub>12</sub>)alkylmethicone copolyol sold by the company Dow Corning under the name Q2 5200;

5                   - substituted and unsubstituted amine groups, such as the products sold under the name GP 4 Silicone Fluid and GP 7100 by the company Genesee, and the products sold under the names Q2 8220 and Dow Corning 929 and 939 by the company Dow Corning. The substituted amine groups are chosen from, for example, C<sub>1</sub>-C<sub>4</sub> aminoalkyl groups;

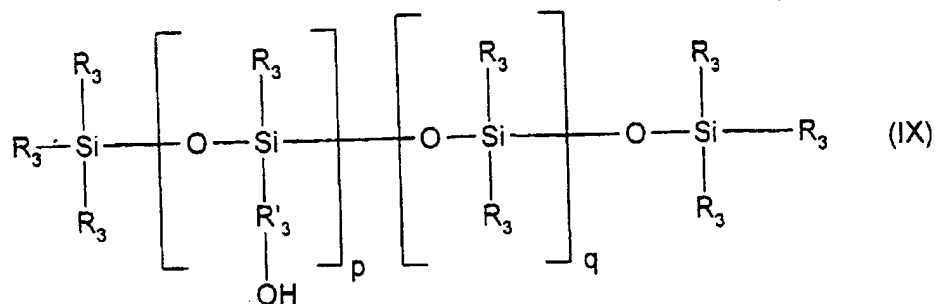
10                   - quaternary ammonium groups, such as the products sold under the names Abilquat 3272 and Abilquat 3474 by the company Goldschmidt;

                  - thiol groups, such as the products sold under the names "GP 72 A" and "GP 71" from Genesee;

15                   - alkoxyated groups, such as the product sold under the name "Silicone Copolymer F-755" by SWS Silicones and Abil Wax 2428, 2434 and 2440 by the company Goldschmidt;

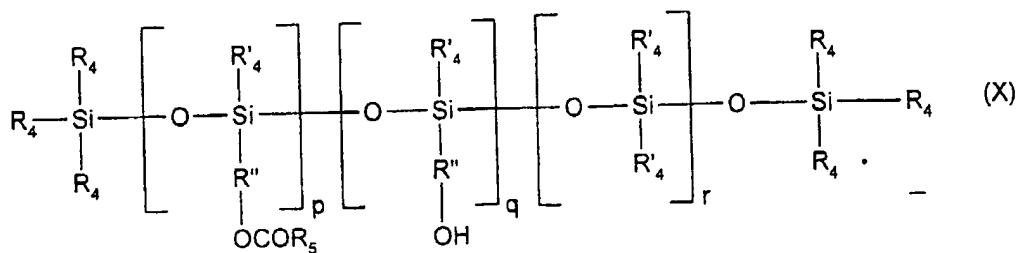
                  - hydroxyalkyl groups, such as the polyorganosiloxanes comprising at least one hydroxyalkyl function, described in French patent application FR-A-85/16334, the disclosure of which is incorporated by reference herein, corresponding to formula (IX):

20



in which the radicals  $\text{R}_3$ , which may be identical or different, are independently chosen from methyl and phenyl radicals, wherein at least 60 mol% of the radicals  $\text{R}_3$  are methyl; the radical  $\text{R}'_3$  is chosen from divalent  $\text{C}_2\text{-C}_{18}$  hydrocarbon-based alkylene chain units;  $p$  ranges from 1 to 30;  $q$  ranges from 1 to 150;

- acyloxyalkyl groups such as, for example, the polyorganosiloxanes described in patent US-A-4,957,732, the disclosure of which is incorporated by reference herein, and corresponding to formula (X):



in which:

$R_4$ , which may be identical or different, are independently chosen from methyl, phenyl, -OCOR<sub>5</sub> and hydroxyl groups, it being possible for only one of the radicals  $R_4$  per silicon atom to be OH;

5  $R'_4$ , which may be identical or different, are independently chosen from methyl and phenyl; and wherein at least 60 mol% of all of the radicals  $R_4$  and  $R'_4$  are chosen from methyl;

$R_5$  is chosen from C<sub>8</sub>-C<sub>20</sub> alkyl and C<sub>8</sub>-C<sub>20</sub> alkenyl groups;

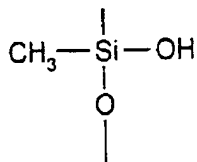
10  $R''$ , which may be identical or different, are independently chosen from linear and branched, divalent C<sub>2</sub>-C<sub>18</sub> hydrocarbon-based alkylene radicals;

$r$  ranges from 1 to 120;

$p$  ranges from 1 to 30;

$q$  ranges from 0 to less than 0.5  $p$ , wherein the sum of  $p + q$  ranges from 1 to 30;

provided that when the polyorganosiloxanes of formula (X) comprise groups:



15 such groups are present in proportions not exceeding 15% of the sum  $p + q + r$ .

- anionic groups of carboxylic type, such as, for example, in the products described in patent EP 186 507, the disclosure of which is incorporated by reference herein, from the company Chisso Corporation, or of alkylcarboxylic type, such as those

present in the product X-22-3701E from the company Shin-Etsu;

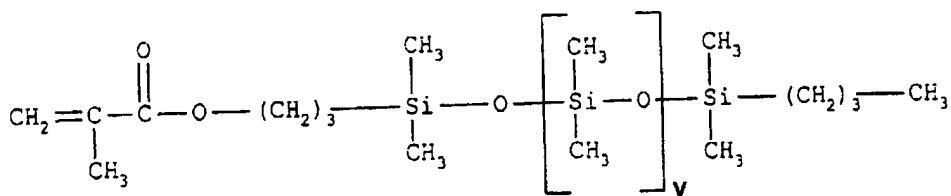
- 2-hydroxyalkyl sulfonate; 2-hydroxyalkyl thiosulfate such as the products sold by the company Goldschmidt under the names "Abil S201" and "Abil S255".

- hydroxyacylamino groups, such as the polyorganosiloxanes described in patent application EP 342 834, the disclosure of which is incorporated by reference herein. Mention may be made, for example, of the product Q2-8413 from the company Dow Corning.

Additional silicones that can also be used according to the invention are silicones comprising a polysiloxane and a non-silicone organic chain, wherein either the polysiloxane or the non-silicone organic chain is considered the main chain of the polymer and the other is grafted onto said main chain. These polymers are described, for example, in patent applications EP-A-412,704, EP-A-412,707, EP-A-640,105, WO 95/00578, EP-A-582,152 and WO 93/23009 and US patents 4,693,935, 4,728,571 and 4,972,037, the disclosures of which are incorporated by reference herein. These polymers are preferably anionic or nonionic.

Such polymers are, for example, copolymers obtained by radical polymerization starting with the monomer mixture comprising:

- a) 50 to 90% by weight of tert-butyl acrylate;
- b) 0 to 40% by weight of acrylic acid;
- c) 5 to 40% by weight of silicone macromer of formula:



with v being a number ranging from 5 to 700; the weight percentages being calculated relative to the total weight of the monomers.

Other examples of grafted silicone polymers are, for example,

polydimethylsiloxanes (PDMS) onto which are grafted, via a connecting chain unit of thiopropylene type, mixed polymer units of poly(meth)acrylic acid type and of polyalkyl (meth)acrylate type and polydimethylsiloxanes (PDMS) onto which are grafted, via a connecting chain unit of thiopropylene type, polymer units of polyisobutyl (meth)acrylate type.

According to the invention, all of the silicones can also be used in a form chosen from emulsions, nanoemulsions and microemulsions.

The polyorganosiloxanes that can be used in accordance with the invention are, for example:

- nonvolatile silicones chosen from (1) polyalkylsiloxanes comprising trimethylsilyl end groups, such as oils with a kinematic viscosity ranging from 0.2 to 2.5 m<sup>2</sup>/s at 25°C, such as the oils of the series DC200 from Dow Corning, for example, one with a viscosity of 60,000 Cst, of the series Silbione 70047 and 47 and more particularly the oil 70 047 V 500 000, which are sold by the company Rhône-Poulenc; (2) polyalkylsiloxanes comprising dimethylsilanol end groups, such as dimethiconol; (3) polyalkylarylsiloxanes such as the oil Silbione 70641 V 200 sold by the company Rhône-Poulenc; (4) the organopolysiloxane resin sold under the name Dow Corning

593; (5) polysiloxanes comprising amine groups, such as amodimethicones and trimethylsilylamodimethicones; and (6) polysiloxanes comprising quaternary ammonium groups.

According to the invention, the at least one additional silicone can be present in an amount ranging from 0.001% to 20% by weight, such as from 0.01% to 10% by weight and further such as from 0.1% to 3% by weight, relative to the total weight of the final composition.

The compositions of the invention can also comprise at least one surfactant chosen from anionic, amphoteric and nonionic surfactants, which is generally present in an amount ranging from approximately 0.1% to 60% by weight relative to the total weight of the composition, such as from 3% to 40% and further such as from 5% to 30%.

The at least one surfactant chosen from anionic, amphoteric and nonionic surfactants, which are suitable for carrying out the present invention are, for example, the following:

(i) Anionic surfactant(s):

In the context of the present invention, their nature is not of critical importance.

Representative anionic surfactants include salts (for example alkaline salts, such as sodium salts, ammonium salts, amine salts, amino alcohol salts and magnesium salts) of the following compounds: alkyl sulfates, alkyl ether sulfates, alkylamidoether sulfates, alkylaryl polyether sulfates, monoglyceride sulfates; alkyl sulfonates, alkyl phosphates, alkylamide sulfonates, alkylaryl sulfonates,  $\alpha$ -olefin sulfonates, paraffin sulfonates; alkyl sulfosuccinates, alkyl ether sulfosuccinates, alkylamide

sulfosuccinates; alkyl sulfosuccinamates; alkyl sulfoacetates; alkyl ether phosphates; acyl sarcosinates; acyl isethionates and N-acyltaurates. The alkyl and acyl radicals of all of these various compounds can for example comprise from 8 to 24 carbon atoms, and the aryl radicals can for example be chosen from phenyl and benzyl groups.

For example, anionic surfactants can be chosen from fatty acid salts such as the salts of oleic, ricinoleic, palmitic and stearic acids, coconut oil acid and hydrogenated coconut oil acid and acyl lactylates in which the acyl radical comprises from 8 to 20 carbon atoms. At least one weakly anionic surfactant can also be used, such as alkyl-D-galactosiduronic acids and their salts, as well as polyoxyalkylenated ( $C_6$ - $C_{24}$ ) alkyl ether carboxylic acids, polyoxyalkylenated ( $C_6$ - $C_{24}$ ) alkylaryl ether carboxylic acids, polyoxyalkylenated ( $C_6$ - $C_{24}$ ) alkylamido ether carboxylic acids and their salts, for example, those comprising from 2 to 50 ethylene oxide groups.

As a further example, the anionic surfactant can be at least one salt chosen from alkyl sulfate salts and alkyl ether sulfate salts.

(ii) Nonionic surfactant(s):

Useful nonionic surfactants include compounds that are well known per se (see for example in this respect "Handbook of Surfactants" by M.R. Porter, published by Blackie & Son (Glasgow and London), 1991, pp. 116-178), the disclosure of which is incorporated by reference herein, and, in the context of the present invention, their nature is not a critical feature. Thus, nonionic surfactants can include polyethoxylated, polypropoxylated and polyglycerolated fatty acids, alkylphenols,  $\alpha$ -diols and alcohols having a fatty aliphatic chain comprising, for example, 8 to 18 carbon atoms, it being possible for the number of ethylene oxide and propylene oxide groups to range for

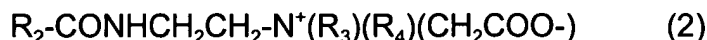
example from 2 to 50 and for the number of glycerol groups to range for example from 2 to 30. Mention may also be made of copolymers of ethylene oxide and of propylene oxide, condensates of ethylene oxide and of propylene oxide with fatty alcohols; polyethoxylated fatty amides for example comprising from 2 to 30 mol of ethylene oxide, polyglycerolated fatty amides comprising on average 1 to 5, such as from 1.5 to 4, glycerol groups; polyethoxylated fatty amines for example comprising from 2 to 30 mol of ethylene oxide; oxyethylenated fatty acid esters of sorbitan comprising from 2 to 30 mol of ethylene oxide; fatty acid esters of sucrose, fatty acid esters of polyethylene glycol, alkylpolyglycosides, N-alkylglucamine derivatives, amine oxides such as (C<sub>10</sub>-C<sub>14</sub>)alkylamine oxides and N-acylaminopropylmorpholine oxides. It will be noted that the alkylpolyglycosides are nonionic surfactants that can be suitable in the context of the present invention.

(iii) Amphoteric surfactant(s):

Representative amphoteric surfactants, whose nature is not a critical feature in the context of the present invention, can be chosen from aliphatic secondary and tertiary amine derivatives in which the aliphatic radical is chosen from linear and branched chain radicals comprising 8 to 22 carbon atoms and comprising at least one water-soluble anionic group (chosen for example from carboxylate, sulfonate, sulfate, phosphate and phosphonate); mention may also be made of (C<sub>8</sub>-C<sub>20</sub>)alkylbetaines, sulfobetaines, (C<sub>8</sub>-C<sub>20</sub>)alkylamido(C<sub>1</sub>-C<sub>6</sub>)alkylbetaines and (C<sub>8</sub>-C<sub>20</sub>)alkylamido(C<sub>1</sub>-C<sub>6</sub>)alkylsulfobetaines.

Representative amine derivatives include the products sold under the name

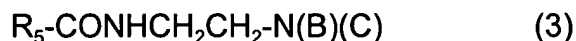
Miranol, as described in US patents 2,528,378 and 2,781,354, the disclosures of which are incorporated by reference herein, and having the structures:



in which:

- $R_2$  is chosen from alkyl radicals derived from an acid  $R_2-COOH$  present in hydrolysed coconut oil, heptyl, nonyl and undecyl radicals,
- $R_3$  is chosen from  $\beta$ -hydroxyethyl groups, and
- $R_4$  is chosen from carboxymethyl groups;

and



in which:

- (B) is  $-CH_2CH_2OX'$ , with  $X'$  chosen from a  $-CH_2CH_2-COOH$  group and a hydrogen atom,
- (C) is  $-(CH_2)_z-Y'$ , with  $z = 1$  or  $2$ , and with  $Y'$  chosen from  $-COOH$  and  $-CH_2-CHOH-SO_3H$  radicals,
- $R_5$  is chosen from alkyl radicals, such as (a) alkyl radicals of an acid  $R_5-COOH$  present in oils chosen from coconut oil and hydrolysed linseed oil, (b) alkyl radicals, such as  $C_7$ ,  $C_9$ ,  $C_{11}$  and  $C_{13}$  alkyl radicals, and (c)  $C_{17}$  alkyl radicals and the iso forms, and unsaturated  $C_{17}$  radicals.

Such representative compounds are classified in the CTFA dictionary, 5th edition, 1993, under the names disodium cocoamphodiacetate, disodium lauroamphodiacetate, disodium caprylamphodiacetate, disodium capryloamphodiacetate, disodium cocoamphodipropionate, disodium

lauroamphodipropionate, disodium caprylamphodipropionate, disodium capryloamphodipropionate, lauroamphodipropionic acid, and cocoamphodipropionic acid.

By way of example, mention may be made of the cocoamphodiacetate sold under the trade name Miranol C2M Concentrate by the company Rhône-Poulenc.

5 In the compositions in accordance with the invention, at least two surfactants of different types can be used. Representative compositions include compositions comprising (a) more than one anionic surfactant, (b) at least one anionic surfactant and at least one amphoteric surfactant, and (c) at least one anionic surfactant and at least one nonionic surfactant. In one embodiment, the composition can comprise at least one  
10 anionic surfactant and at least one amphoteric surfactant.

The at least one anionic surfactant used for example, can be chosen from (C<sub>12</sub>-C<sub>14</sub>)alkyl sulfates of sodium, of triethanolamine and of ammonium; (C<sub>12</sub>-C<sub>14</sub>)alkyl ether sulfates of sodium, of triethanolamine and of ammonium, oxyethylenated with 2.2 mol of ethylene oxide; sodium cocoyl isethionate; and sodium (C<sub>14</sub>-C<sub>16</sub>)- $\alpha$ -olefin sulfonate,  
15 and used in combination with an amphoteric surfactant chosen from either:

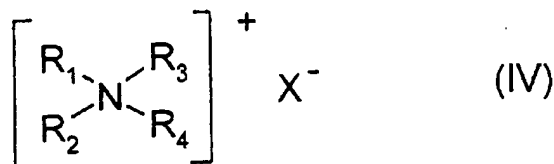
- amphoteric surfactants such as the amine derivatives known as disodium cocoamphodipropionate and sodium cocoamphopropionate, sold for example by the company Rhône-Poulenc under the trade name "Miranol C2M Conc®" as an aqueous solution comprising 38% active material, and under the name Miranol C32; or  
20 - amphoteric surfactants of zwitterionic type, such as alkylbetaines, for example the cocobetaine sold under the name "Dehyton AB 30" as an aqueous solution comprising 32% AM by the company Henkel.

In one embodiment of the invention, the compositions can also comprise at least one cationic surfactant.

Representative at least one cationic surfactants can be chosen from salts of optionally polyoxyalkylenated primary, secondary and tertiary fatty amines; quaternary ammonium salts; imidazoline derivatives; and amine oxides of cationic nature.

The cationic surfactants may, for example, be chosen from:

A) quaternary ammonium salts of formula (IV) below:



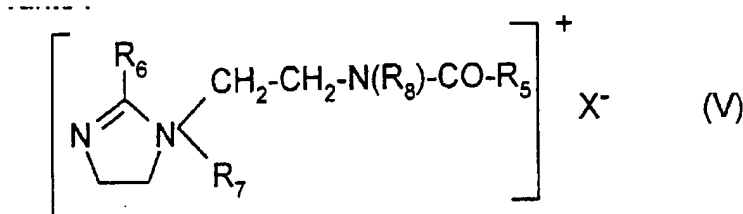
in which:

- the radicals  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$ , which may be identical or different, are independently chosen from linear and branched aliphatic radicals comprising from 1 to 30 carbon atoms, and aromatic radicals, such as  $C_6$ - $C_{20}$  aromatic radicals (for example, aryl and alkylaryl), wherein the aliphatic radicals can comprise hetero atoms such as, oxygen, nitrogen, sulfur and halogens, and wherein the aliphatic radicals are chosen, for example, from alkyl, alkoxy, polyoxy( $C_2$ - $C_6$ )alkylene, alkylamide, ( $C_{12}$ - $C_{22}$ )alkylamido( $C_2$ - $C_6$ )alkyl, ( $C_{12}$ - $C_{22}$ )alkylacetate and hydroxyalkyl radicals, comprising from 1 to 30 carbon atoms;

- X<sup>-</sup> is an anion chosen from halides, phosphates, anions derived from organic acids, (C<sub>2</sub>-C<sub>6</sub>)alkyl sulfates, alkyl sulfonates, and alkylaryl sulfonates.

The compounds of formula (IV) can be chosen from, for example, (a) compounds comprising at least two fatty aliphatic radicals comprising from 8 to 30 carbon atoms, (b) compounds comprising at least one fatty aliphatic radical comprising from 17 to 30 carbon atoms, and (c) compounds comprising at least one aromatic radical.

B) Quaternary ammonium salts of imidazolinium, such as, for example, the salts of formula (V) below:



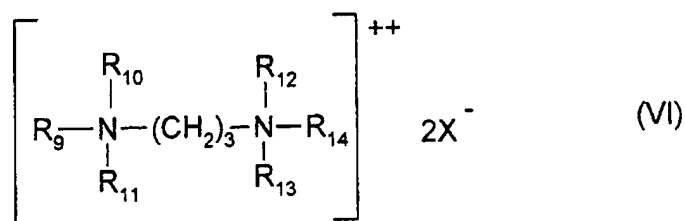
in which:

- R<sub>5</sub> is chosen from alkenyl and alkyl radicals comprising from 8 to 30 carbon atoms, for example radicals derived from tallow fatty acid,
- R<sub>6</sub> is chosen from a hydrogen atom, C<sub>1</sub>-C<sub>4</sub> alkyl radicals, and alkenyl and alkyl radicals comprising from 8 to 30 carbon atoms,
- R<sub>7</sub> is chosen from C<sub>1</sub>-C<sub>4</sub> alkyl radicals,
- R<sub>8</sub> is chosen from a hydrogen atom and C<sub>1</sub>-C<sub>4</sub> alkyl radicals,
- X<sup>-</sup> is an anion chosen from halides, phosphates, acetates, lactates, alkyl sulfates, alkyl sulfonates, and alkylaryl sulfonates.

- For example,  $R_5$  and  $R_6$ , which may be identical or different, are independently chosen from alkenyl and alkyl radicals comprising from 12 to 21 carbon atoms, for example, radicals derived from tallow fatty acid,
- $R_7$  is methyl, and
- $R_8$  is hydrogen.

Such products are, for example, (1) Quaternium-27 (International Cosmetic Ingredient Dictionary and Handbook, hereafter "CTFA", 1997), i.e., "Rewoquat" W75, W75PG, and W90, and (2) Quaternium-83 (CTFA 1997), i.e., "Rewoquat" W75HPG, which are sold by the company Witco.

C) Diquaternary ammonium salts of formula (VI):



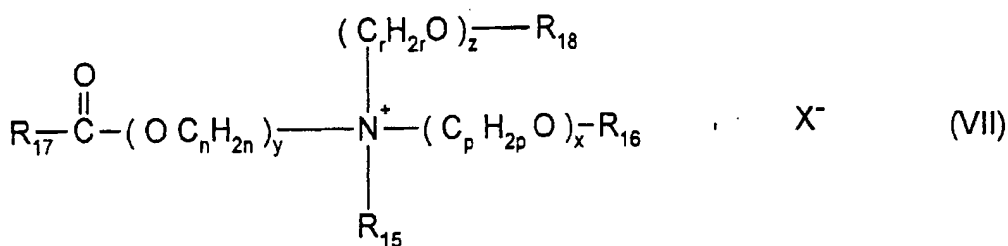
in which:

- $R_9$  is chosen from aliphatic radicals comprising from 16 to 30 carbon atoms,
- $R_{10}$ ,  $R_{11}$ ,  $R_{12}$ ,  $R_{13}$  and  $R_{14}$ , which may be identical or different, are independently chosen from a hydrogen atom and alkyl radicals comprising from 1 to 4 carbon atoms, and

- X<sup>-</sup> is an anion chosen from halides, acetates, phosphates, nitrates and methyl sulfates.

For example, such diquaternary ammonium salts can comprise propane tallow diammonium dichloride.

5 D) Quaternary ammonium salts comprising at least one ester function. The quaternary ammonium salts comprising at least one ester function that can be used according to the invention are, for example, those of formula (VII) below:

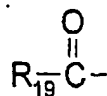


in which:

- R<sub>15</sub> is chosen from C<sub>1</sub>-C<sub>6</sub> alkyl radicals and C<sub>1</sub>-C<sub>6</sub> hydroxyalkyl and C<sub>1</sub>-C<sub>6</sub> dihydroxyalkyl radicals;

- R<sub>16</sub> is chosen from:

- acyl groups of the following formula:



wherein R<sub>19</sub> is defined below,

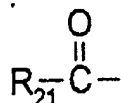
- linear and branched, saturated and unsaturated, C<sub>1</sub>-C<sub>22</sub>

hydrocarbon-based radicals, and

- a hydrogen atom;

- R<sub>18</sub> is chosen from:

- acyl groups of the following formula:



wherein R<sub>21</sub> is defined below,

- linear and branched, saturated and unsaturated, C<sub>1</sub>-C<sub>6</sub>

hydrocarbon-based radicals, and

- a hydrogen atom;

- R<sub>17</sub>, R<sub>19</sub> and R<sub>21</sub>, which may be identical or different, are independently chosen from linear and branched, saturated and unsaturated, C<sub>7</sub>-C<sub>21</sub> hydrocarbon-based radicals;

- n, p and r, which may be identical or different, are independently integers ranging from 2 to 6;

- y is an integer ranging from 1 to 10;

- x and z, which may be identical or different, are independently integers ranging from 0 to 10;

-  $X^-$  is chosen from simple and complex, organic and inorganic anions;

- provided that the sum  $x + y + z$  is from 1 to 15, and that when x is 0, then  $R_{16}$  is chosen from linear and branched, saturated and unsaturated,  $C_1$ - $C_{22}$

hydrocarbon-based radicals, and that when z is 0, then  $R_{18}$  is chosen from linear and branched, saturated and unsaturated,  $C_1$ - $C_6$  hydrocarbon-based radicals.

In one embodiment, the  $R_{15}$  alkyl radicals may be linear and branched and further, for example, linear.

For example,  $R_{15}$  may be chosen from methyl, ethyl, hydroxyethyl and dihydroxypropyl radicals and further for example from methyl and ethyl radicals.

The sum  $x + y + z$  may for example range from 1 to 10.

When  $R_{16}$  is chosen from linear and branched, saturated and unsaturated,  $C_1$ - $C_{22}$  hydrocarbon-based radicals,  $R_{16}$  may be long and comprise from 12 to 22 carbon atoms, or short and comprise from 1 to 3 carbon atoms.

When  $R_{18}$  is chosen from linear and branched, saturated and unsaturated,  $C_1$ - $C_6$  hydrocarbon-based radicals,  $R_{18}$  may for example comprise from 1 to 3 carbon atoms.

$R_{17}$ ,  $R_{19}$  and  $R_{21}$ , which may be identical or different, can, for example, be independently chosen from linear and branched, saturated and unsaturated  $C_{11}$ - $C_{21}$  hydrocarbon-based radicals, and for example from linear and branched, saturated and unsaturated,  $C_{11}$ - $C_{21}$  alkyl and alkenyl radicals.

x and z, which may be identical or different, can for example independently be chosen from 0 or 1.

y for example may be equal to 1.

n, p and r, which may be identical or different, can for example be independently chosen from 2 and 3 and in one embodiment equal to 2.

The anion for example can be chosen from halides (chloride, bromide, and iodide) and alkyl sulfates, such as methyl sulfate. However, methanesulfonate, phosphate, nitrate, tosylate, anions derived from organic acids, such as acetate and lactate, and any other anions compatible with the ammonium comprising an ester function, may be used.

As a further example, the anion  $X^-$  can be chosen from chloride and methyl sulfate.

Further examples of ammonium salts of formula (VII) are those in which:

- $R_{15}$  is chosen from methyl and ethyl radicals,
- x and y are equal to 1;
- z is equal to 0 or 1;
- n, p and r are equal to 2;
- $R_{16}$  is chosen from:



wherein  $R_{19}$  is defined below,

- methyl, ethyl and  $C_{14}$ - $C_{22}$  hydrocarbon-based radicals, and

- a hydrogen atom;

- R<sub>18</sub> is chosen from:

- acyl radicals  $R_{21}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-$

- wherein R<sub>21</sub> is defined below,

- a hydrogen atom;

- R<sub>17</sub>, R<sub>19</sub> and R<sub>21</sub>, which may be identical or different, are independently chosen from linear and branched, saturated and unsaturated, C<sub>13</sub>-C<sub>17</sub> hydrocarbon-based radicals, such as from linear and branched, saturated and unsaturated C<sub>13</sub>-C<sub>17</sub> alkyl and alkenyl radicals.

The hydrocarbon-based radicals can for example be linear.

Representative compounds of formula (VII) are chosen from diacyloxyethyl-dimethylammonium, diacyloxyethylhydroxyethylmethylammonium, monoacyloxyethyldihydroxyethylmethylammonium, triacyloxyethylmethylammonium and monoacyloxyethylhydroxyethyldimethylammonium salts (for example chloride and methyl sulfate). The acyl radicals can for example comprise from 14 to 18 carbon atoms and can for example be obtained from plant oils, such as palm oil and sunflower oil. When the compound comprises several acyl radicals, these radicals, which may be independently chosen, may independently be identical or different.

These products are obtained, for example, by direct esterification of compounds chosen from triethanolamine, triisopropanolamine, alkyldiethanolamines and

alkyldiisopropanolamines, which are optionally oxyalkylenated, with fatty acids or with fatty acid mixtures of plant or animal origin, and by transesterification of the methyl esters thereof. This esterification is followed by a quaternization using an alkylating agent such as alkyl halides (such as methyl and ethyl halides), dialkyl sulfates (for example dimethyl and diethyl sulfates), methyl methanesulfonate, methyl para-toluenesulfonate, glycol chlorohydrin and glycerol chlorohydrin.

Such compounds are sold, for example, under the names Dehyquat by the company Henkel, Stepanquat by the company Stepan, Noxamium by the company Ceca and Rewoquat WE 18 by the company Rewo-Witco.

It is also possible to use the ammonium salts comprising at least one ester function, described in patents US-A-4 874 554 and US-A-4 137 180, the disclosures of which are incorporated by reference herein.

Representative quaternary ammonium salts of formula (IV) include tetraalkylammonium chlorides such as, for example, dialkyldimethylammonium chlorides and alkyltrimethylammonium chlorides, in which the alkyl radical comprises from 12 to 22 carbon atoms, for example behenyltrimethylammonium chloride, distearyldimethylammonium chloride, cetyltrimethylammonium chloride, and benzyldimethylstearylammonium chloride, and, stearamidopropyldimethyl(myristyl acetate)ammonium chloride sold under the name "Cepharyl 70" by the company Van Dyk.

According to the invention, the at least one cationic surfactant can for example be present in an amount ranging from 0.1% to 20% by weight relative to the total weight

of the final composition, such as from 0.1% to 10%, from 0.5% to 7%, and further such as from 1% to 5% by weight relative to the total weight of the final composition.

5 The composition of the invention can also comprise at least one additive chosen from thickeners, fragrances, nacreous agents, preserving agents, silicone sunscreens, non-silicone sunscreens, vitamins, provitamins, cationic, amphoteric, anionic and nonionic polymers, proteins, protein hydrolysates, 18-methyleicosanoic acid, hydroxy acids, panthenol, ceramides, pseudoceramides, plant, animal, mineral and synthetic oils and any other additive conventionally used in cosmetics which does not substantially adversely affect the properties of the compositions according to the invention.

10 Generally, these additives are present in the composition according to the invention in amounts, for example, ranging from 0 to 20% by weight relative to the total weight of the composition. The precise amount of each additive is readily determined by those skilled in the art depending on its nature and its function.

15 The compositions in accordance with the invention can also be used for washing or treating at least one keratin material chosen from hair, skin, eyelashes, eyebrows, nails, lips, scalp, and hair.

20 The compositions according to the invention can also be a detergent composition chosen from shampoos, shower gels, bubble baths and make-up-removing products. In this embodiment of the invention, the compositions comprise a washing base, which is generally aqueous.

At least one surfactant forms the washing base and can be chosen from anionic, amphoteric, nonionic and cationic surfactants, such as those defined above.

The quantity and quality of the washing base are sufficient to give the final composition at least one of the following qualities, satisfactory foaming power and satisfactory detergent power.

According to the invention, the washing base can be present for example in an amount ranging from 4% to 50% by weight, such as from 6% to 35% by weight and even further such as from 8% to 25% by weight, relative to the total weight of the final composition.

Another subject of the invention is also a process for treating at least one keratin material, such as the skin and the hair, comprising applying a cosmetic composition as defined above to the at least one keratin material and optionally rinsing it out with water.

Thus, this process according to the invention allows maintenance of the hairstyle and treatment of, care of, washing of or removal of make-up from the skin, the hair or any other keratin material.

The compositions of the invention can for example be in forms chosen from rinse-out conditioners and leave-in conditioners; permanent-waving, straightening, dyeing and bleaching compositions; rinse-out compositions to be applied before a procedure chosen from dyeing, bleaching, permanent-waving and straightening the hair; rinse-out compositions to be applied after a procedure chosen from dyeing, bleaching, permanent-waving and straightening the hair; and rinse-out compositions to be applied between the two steps of a procedure chosen from permanent-waving and straightening the hair.

The compositions according to the invention can also be in a form chosen from aqueous and aqueous-alcoholic lotions for a care chosen from skin care and hair care.

The cosmetic compositions according to the invention can be in a form chosen from gels, milks, creams, emulsions, thickened lotions and mousses and can be used for treating at least one keratin material chosen from skin, nails, eyelashes, lips, and hair.

5           The compositions can be packaged in various forms chosen from vaporizers, pump-dispenser bottles and aerosol containers in order to ensure application of the composition in vaporized form or in the form of a mousse. Such packaging forms are indicated, for example, when it is desired to obtain a spray, a lacquer or a mousse for treating the hair.

10           In all of the text hereinabove and hereinbelow, the percentages expressed are on a weight basis.

          The invention will now be illustrated more fully with the aid of the examples which follow, which should not be considered as limiting it to the embodiments described. In the examples, AM means active material.

15           EXAMPLE 1

          A conditioner in accordance with the invention, having the following composition, was prepared:

- |  |        |
|--|--------|
| - Mixture of myristyl, cetyl and stearyl myristate, palmitate and stearate | 1 g    |
| - Cetyl alcohol  | 5 g    |
| - Hydroxyethylcellulose (MW 1,300,000)                                     | 0.25 g |
| - Behenyltrimethylammonium chloride (Genamin KDMP from Clariant)           | 1 g AM |

- Cationic emulsion containing 67% AM of copolymer of polydimethylsiloxane containing  $\alpha,\omega$ -vinyl groups/polydimethylsiloxane containing  $\alpha,\omega$ -hydrogeno groups (DC-1997 from Dow Corning) 0.8 g AM 5 g
- Polydimethylsiloxane (Mirasil DM300 from Rhodia Chimie)
- Polydimethylsiloxane (DC200 Fluid-60,000 CS from Dow Corning) 1 g
- Fragrance, preserving agents qs
- Water qs 100 g

This composition is applied to washed and dried hair. It is left to stand on the hair for 2 minutes and is then rinsed off with water.

Hair treated with this conditioner is soft, smooth and disentangles easily.

## EXAMPLE 2

A conditioner in accordance with the invention, having the following composition, was prepared:

- Cationic emulsion containing 67% AM of copolymer of polydimethylsiloxane containing  $\alpha,\omega$ -vinyl groups/polydimethylsiloxane containing  $\alpha,\omega$ -hydrogeno groups (DC-1997 from Dow Corning) 0.7 gAM
- SMDI/polyethylene glycol/alkyl (methyl/C18) endings copolymer at a concentration

of 15% in a maltodextrin/water matrix

(Aculyn 46 from Rohm & Haas)

0.45 gAM

- crosslinked ethyltrimethylammonium  
methacrylate chloride homopolymer as a

5 reverse emulsion at a concentration of  
50% in mineral oil (Salcare SC 95 from

Ciba Geigy)

0.55 gAM

- Polydimethylsiloxane (Mirasil DM50 from

Rhodia Chimie)

1 g

10 - Mixture of cetyl alcohol and of stearyl  
alcohol (50/50 by weight)

6 g

- Fragrance, preserving agents

qs

- Water

qs

100 g